RADC-TR-89-203
In-House Report
October 1989

AD-A224 487

A COMPARATIVE STUDY OF THREE COMMERCIAL INDIUM PHOSPHIDE SUBSTRATES

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REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	OCT 89	In-house 26 AUG 88 - 1 APR 89

4. TITLE AND SUBTITLE
A Comparative Study of Three Commercial Indium Phosphide Substrates

5. FUNDING NUMBERS
PE - 62702F
PR - 4600
TA - 17
WU - 07

6. AUTHOR(S)
Quinlan, Kenneth P.

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Rome Air Development Center
RADC/ESME
Hanscom AFB
Massachusetts 01731-5000

8. PERFORMING ORGANIZATION REPORT NUMBER
RADC-TR-89-203

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT
APPROVED FOR PUBLIC RELEASE; DISTRIBUTION UNLIMITED

12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

A comparative study of the three commercial indium phosphide substrates, CrystaComm, ICI Americas and Sumitomo Electric, was performed using chemical etching techniques. The average dislocation densities were found to be equal to or slightly greater than the values reported by the manufacturers. All three substrates exhibited speckles and unspecified defects with bromine-methanol etching. The unspecified defect densities were similar for all substrates. Small amounts of subsurface was observed on all wafers. The study showed that the three commercial substrates were of comparable defect density. Results of the study indicate that additional research is necessary in order to improve the technology for preparing InP substrates.

14. SUBJECT TERMS
InP Substrates, InP Wafers, III-V Semiconductors

15. NUMBER OF PAGES
24

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	SAR

Preface

The author wishes to thank Dr. Brian S. Ahern for many helpful suggestions and discussions.

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A Comparative Study of Three Commercial Indium Phosphide Substrates

1. INTRODUCTION

Epitaxial layers of III-V semiconductors lattice-matched to indium phosphide substrates are extremely important structures in optoelectronic and microwave devices such as photodetectors, lasers, MODFET's, bipolar transistors and MISFET's. The performance of these devices is markedly influenced by the presence of defects and damage on the substrates on which the epitaxial layers are deposited.[1,2] The far-reaching versatility of the layered structures has increased the number of suppliers producing indium phosphide substrates. A question arises whether the quality of the substrates produced by the different manufacturers is the same.

This study reports the results of an investigation to determine whether any difference in defects or subsurface damage exists between substrates produced by three manufacturers. Chemical etching procedures were the primary tools used in the experimental approach. The assessment of the substrates comprised the following: 1) The dislocation densities of the

(Received for publication 3 November 1989)

[1] Olsen, G.H., and Zamerowski, T.J. (1980) in *Progress in Crystal Growth and Characterization*, B.R. Pamplin, Editor, p. 309, Pergamon Press Ltd., London.

[2] Caldwell, P.J., Laidig, W.D., Lin, Y.F., Peng, C.K., Magee, T.J. and Leung, C. (1985) *J. Appl. Phys.*,**57**:984.

substrates as received, 2) The morphology of the wafers after a standard etch procedure using various concentrations of bromine in methanol and 3) Subsurface damage.

2. EXPERIMENTAL

The substrates used in the present study are listed in Table 1 with their properties. The 50 mm wafers cut from LEC boules were polished on one side and possessed specular surfaces. The wafers were received in quantities of three from the manufacturer. All chemicals were certified A.C.S. reagent grade. Surfaces were examined with an optical microscope furnished with Nomarski interference contrast equipment.

Table 1. Substrates Studied.

Source	Crystal No.	Dopant	Orientation	E.P.D.
CrystaComm	4198	Fe	(100)3° → (110)	$< 2X10^4$
ICI Americas	RI/209	Fe	(100)2° → (110)	$4X10^4$
Sumitomo	803723-014	Fe	(100)2°→ (110)	$\leq 5X10^4$

2.1 Dislocation Etching

The etchant used to reveal the dislocations was that of Huber and Linh.[3] The etchant consisted of 2 volumes of phosphoric acid (85 percent) and 1 volume of hydrobromic acid (48 percent). The substrates were degreased with toluene, trichloroethane and acetone. The samples, washed with distilled water, were etched at room temperature in the H_3PO_4-HBr solutions for 2 minutes. The substrates were rinsed with water and finally with methanol. The etched substrates were blown dry with helium.

The dislocation densities of the substrates were determined across the center diameter in the <011> direction. The count of dislocations was determined from a series of micrographs characterizing 0.5 X 0.4 mm of the surface. The number of micrographs inspected along the diameter ranged from 11 to 22 for each wafer.

[3] Huber, A. and Linh, N.T. (1975) *J. Crystal Growth*, **29**:80.

2.2 Pre-Epitaxy Etching

The polish etching of InP substrates was accomplished by a standard etch procedure reported earlier.[4,5] The substrates were degreased with toluene, trichloroethane and finally with acetone. The substrates were washed with water and then etched for 5 minutes in Caro's acid (5 vol H_2SO_4 + 1 vol H_2O_2 + 1 vol H_2O). After washing with water and methanol, the substrates were etched for 2 minutes in a bromine-methanol solution. Various concentrations of bromine in methanol were studied. Following the bromine-methanol etch, the substrates were once again etched for 5 minutes in Caro's acid. This etch was followed by water and methanol rinses. The substrates were blown dry with helium.

The amount (μm) of the InP removed by etching was determined from the surface area of the substrate, density of InP and the mass removed by the etchant.

2.3 Subsurface Damage

Substrate damage, for example, scratch marks, swirls and unspecified structures, was evaluated with Chu's etch.[6] Chu's etch contains 3 volumes hydrobromic acid (48 percent) and 1 volume nitric acid (70 percent). Chin and Barlow[7] demonstrated that this solution is the best etchant for detecting subsurface damage. Initially, the samples were degreased as above and rinsed with methanol and distilled water. The substrate samples were then etched for 2 seconds with Chu's etch. The samples were washed with water, methanol and blown dry. The subsurface damage was delineated with a Nomarski Interference Microscope. The average number of scratches, swirls and unspecified structures on the three commercial substrates were determined from samples from the center of three different wafers from each source. The areas of the center pieces were approximately 0.4 cm^2.

The depth of the subsurface damage was determined using the approach of Tuck et al.[8,9] These investigators showed that the depth of the subsurface damage could be determined by studying the etch rate as a function of substrate depth. The depth of the subsurface damage was correlated with the onset of the steady-state etch rate. The degreased samples were rinsed with methanol and distilled water. The samples, held by plastic tweezers, were shaken for

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4 Olsen, G.H. and Zamerowski, T.J. (1981) *IEEE J. Quantum Electron.*, **QE-17**, pp. 128-138.

5 Erstfeld, T.E. and Quinlan, K.P. (1982) *J. Electron. Mater.*, **11**:647.

6 Chu, S.N.G., Jodlauk, C.M. and Ballman, A.A. (1982) *J.Electrochem. Soc.*, **129**:352.

7 Chin, B.H. and Barlow, K.L. (1988) *J. Electrochem. Soc.*, **135**:3120.

8 Tuck, B. and Baker, A.J. (1973) *J. Mater. Sci.*, **8**:1559.

9 Tuck , B.(1975) *J. Mater. Sci.*, **10**:321.

various times in a 0.1 vol % bromine-methanol etch maintained at 25.0 ± 0.1°C. The samples were rinsed with water and methanol, and blown dry. The etch rate was determined from the loss of mass, density of InP, surface area and etch time. Etch rates at different depths were determined with the same sample.

3. RESULTS AND DISCUSSION

The dislocation densities across the three commercial wafers are shown graphically in Figure 1. The dislocations originate from a slip on the {111} planes in the <110> directions. The dislocation pits were either conical or of the shallow flat bottomed type. The etched features of the pits have been classified by Brown et al.[10,11] The ICI Americas and Sumitomo substrates gave the typical "W" shaped curves as predicted from the analysis of Jordan et al.[12] for dislocation generation in GaAs. The CrystaComm wafers exhibit a simple "U" shaped dislocation curve. Different wafers of the CrystaComm and Sumitomo substrates exhibited similar results. The difference in the shape of the curves (Figure 1) is most probably due to the fact that the wafers were obtained from different areas of the boule. Chen et al.[13] obtained similar curves for GaAs. The front-end slices exhibited simple "U" shaped dislocation density curves. The "W" shape of the dislocation density curves became more apparent as the tail-end of the boule was approached. The average dislocation densities found for the CrystaComm, ICI Americas and Sumitomo wafers were 4×10^4, 7×10^4 and $5 \times 10^4/cm^2$, respectively. The CrystaComm and ICI Americas results are slightly higher than those reported (see Table 1) by the manufacturer. The dislocation density determined for the Sumitomo wafers agrees with the reported value. These slight differences between the determined dislocation densities and those reported may also be caused by the comparison being made between wafers from different areas of the boule. These dislocation studies show that the wafers from the three commercial sources exhibited no great deviation from each other.

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[10] Brown, G.T., Cockayne, B. and MacEwan, W.R. (1980) *J. Mater. Sci.*, **15**:2539.

[11] Brown, G.T., Cockayne, B. and MacEwan, W.R. (6-10 April 1981) Microsc. Semicond. Mater. Conf., Inst. Phys. Conf., Ser. No. 60, Section 7, Oxford, pp. 351-356.

[12] Jordan, A.S., Caruso, R. and Von Neida, A.R. (1980) *Bell System Tech. J.*, **59**:593.

[13] Chen, R.T. and Holmes, D.E. (1983) *J. Crystal Growth*, **61**:111.

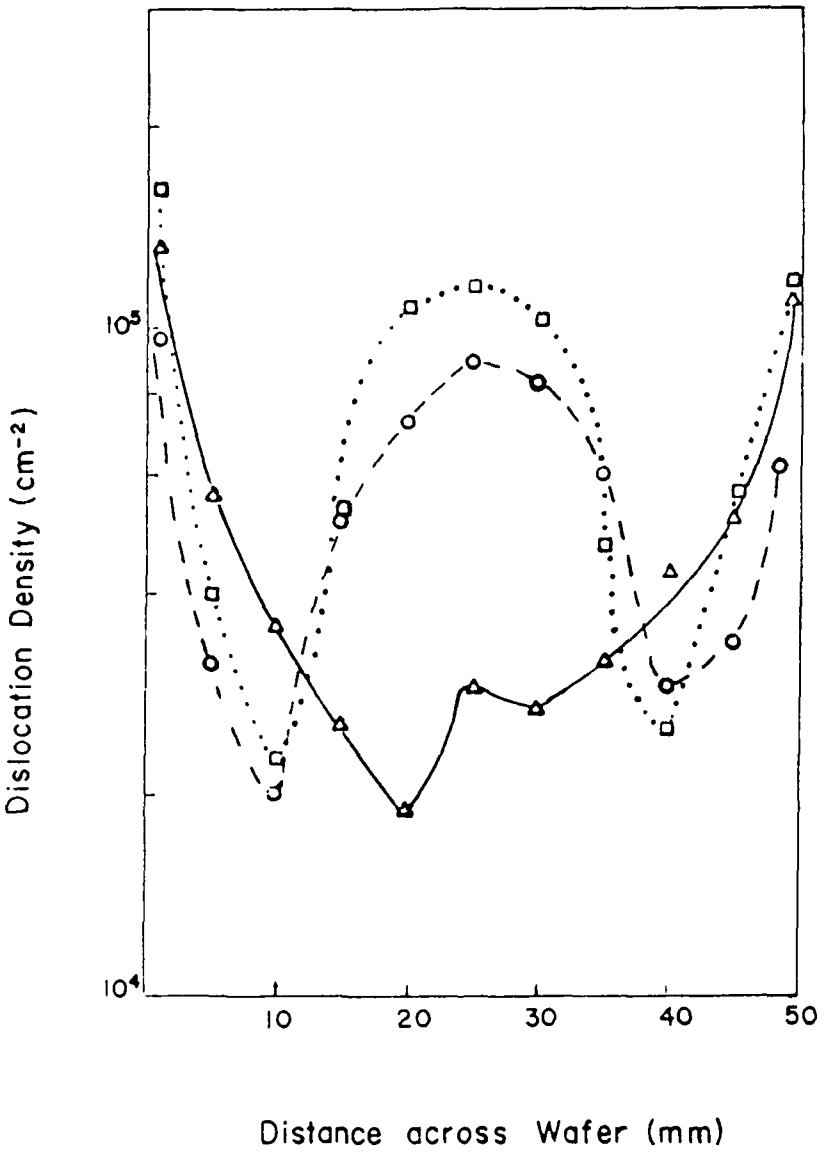


Figure 1. Dislocation Densities Across Diameters of Wafers in the <011> Direction for Three Commercial Substrates: Δ-Δ, CrystaComm; 0-0, Sumitomo Electric; and □-□, ICI Americas.

The substrates were further evaluated with the standard etching procedure described in the experimental section. After degreasing, Caro's acid (5:1:1) treatment of the three substrates produced surfaces with excellent morphology. This Caro's acid treatment of the InP substrate removes 0.16 μm. Salètes et al.[14] advocate the use of Caro's acid (2:1:1) as a polish etch for InP substrates. This Caro's acid treatment probably does not remove all the subsurface damage. The effect of various concentrations of bromine in methanol on the substrates was studied after the Caro's acid etch. The etching time with the bromine-methanol solution was maintained at 2 minutes. Figure 2 shows the amount of InP etched after the standard etch procedure (see Experimental). The amount of InP etched agrees with the magnitude predicted from the etch rates reported by Tuppen et al.[15] but are lower than those of Adachi et al.[16] who studied the (001) orientation. Lower concentrations of bromine in methanol (< 1.5 vol %) produced pocks (speckles) on the surfaces. These speckles are depicted in Figure 3. All the substrates studied reacted to this etching in similar fashion. Speckles were not observed when the amount of bromine in methanol was equal to or greater than 1.5 vol %. This concentration corresponded to the removal of 6 μm of InP. These speckles can be eliminated at lower concentrations of bromine if longer times or higher temperatures are employed. Speckles probably result from the slow oxidation rate of the surface with low concentrations of bromine in methanol.

[14] Salètes, A., Turco, F., Massies, J. and Contour, J.P. (1988) *J. Electrochem. Soc.*, **135**:504.

[15] Tuppen, C.G. and Conen, B.H. (1987) *J. Crystal Growth*, **80**:459.

[16] Adachi, S., Kawaguchi, H. and Iwane, G. (1982) *J.Electrochem. Soc.*, **129**:883.

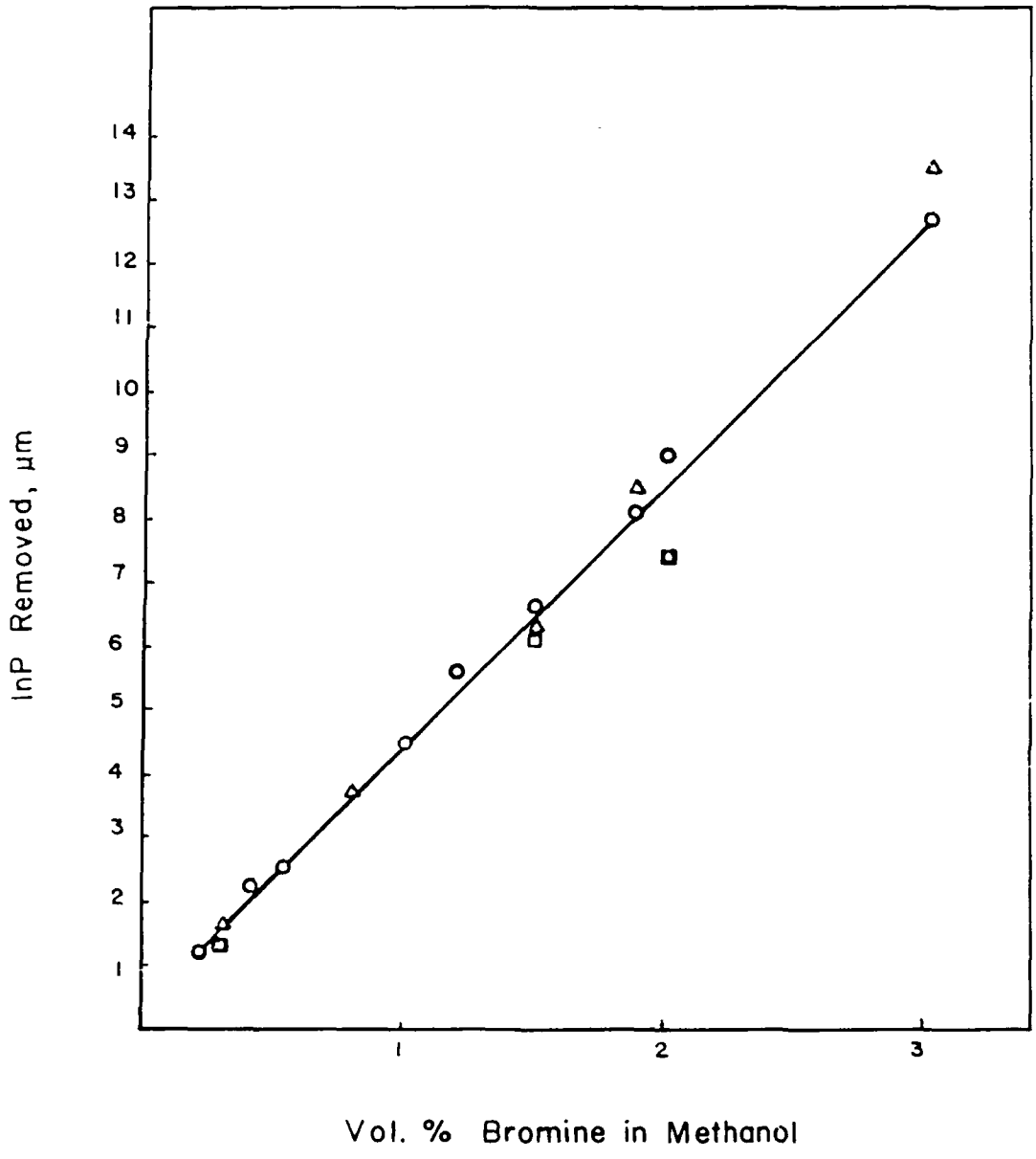


Figure 2. Amount (µm) of InP Etched from Commercial Substrates with Standard Etch Procedure (see Experimental) Using Various Concentrations of Bromine in Methanol for 2 Minutes: 0-0, CrystaComm; Δ-Δ, ICI Americas; and □-□, Sumitomo Electric.

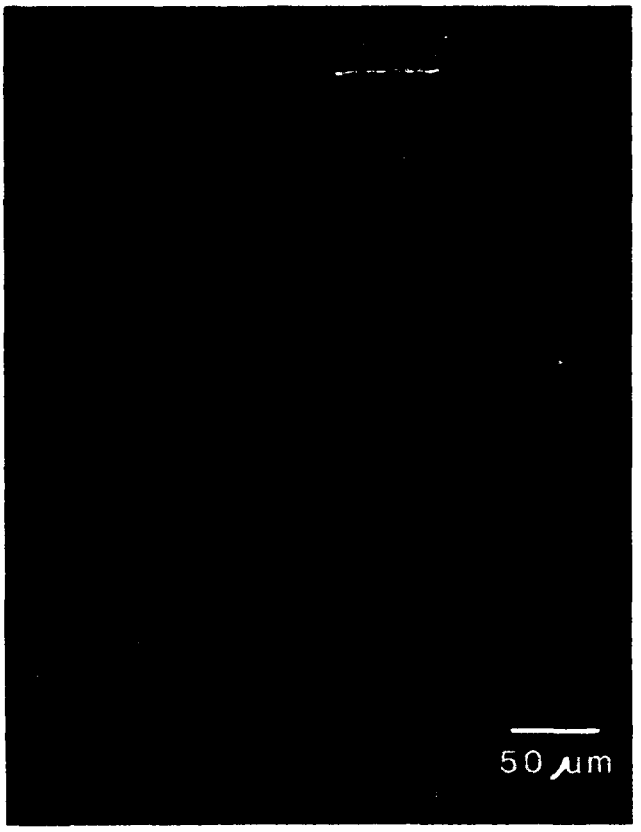
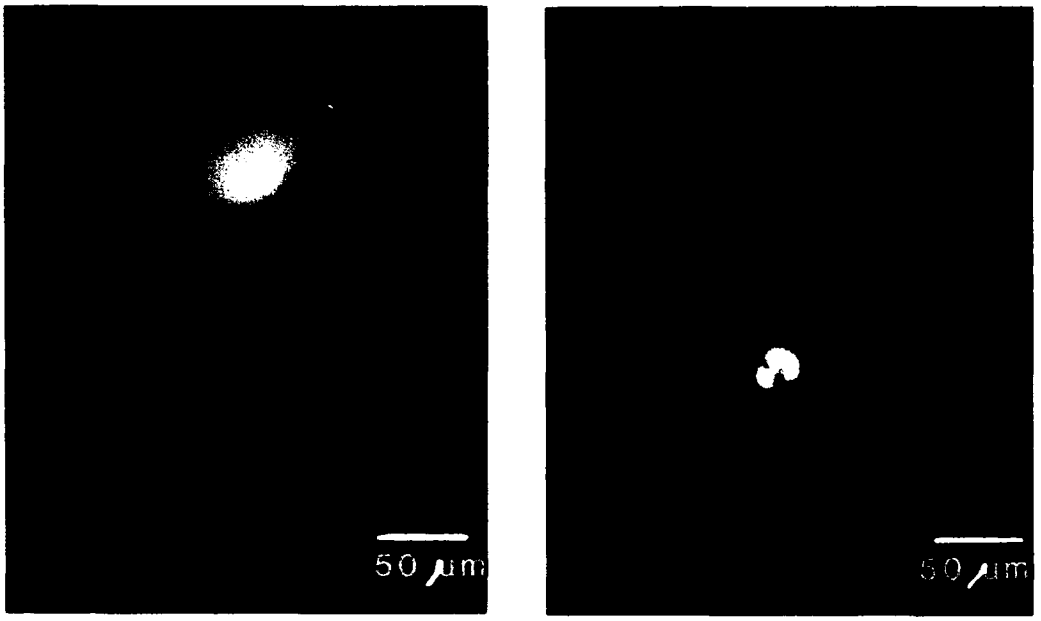


Figure 3. Speckles (Pocks) on InP Substrate Surfaces. Photomicrograph of CrystaComm InP substrate etched for 2 minutes with the standard etch procedure using 0.3 vol % bromine in methanol.

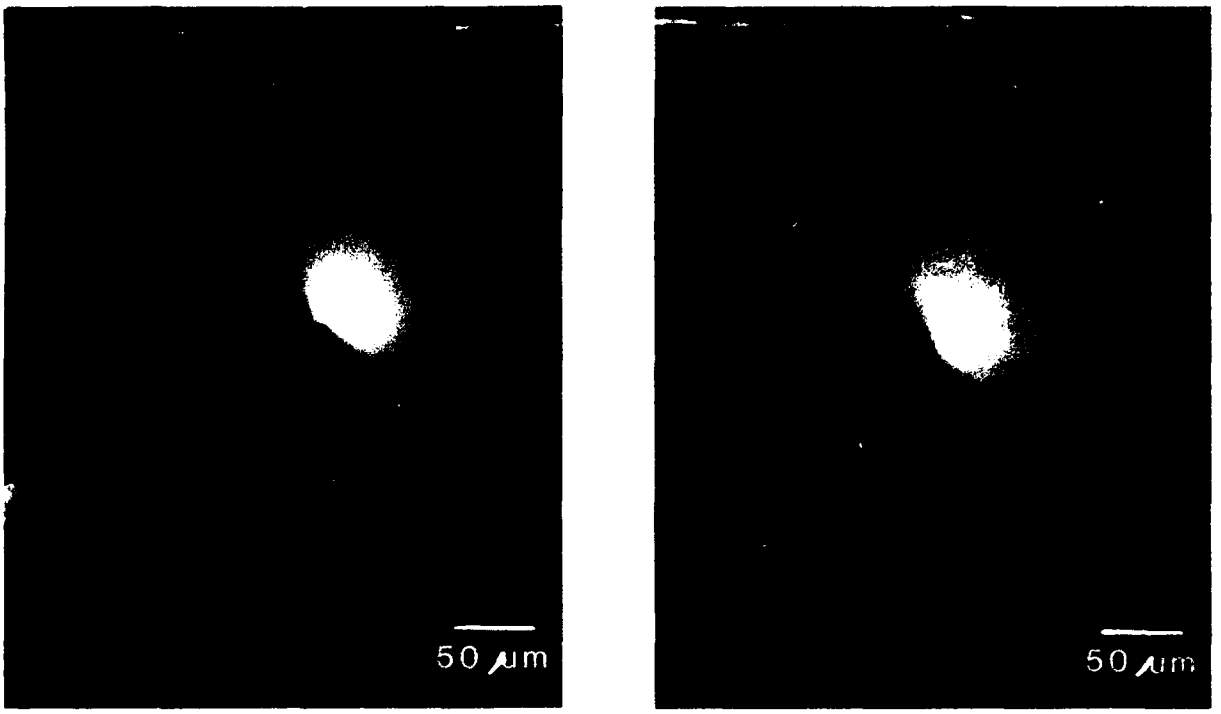
Etching of the three substrates with the standard etch procedure revealed an unspecified type defect. Examples of these unspecified defects are depicted in the photomicrographs of Figure 4. These defects were observed on all the substrates in the complete range of



(a) (b)

Figure 4. Unspecified Defects on InP Substrate Surfaces. a) Photomicrograph of CrystaComm InP substrate after 2 etchings for 2 minutes each with the standard etch procedure using 3 vol % bromine in methanol; b) Photomicrograph of Sumitomo InP substrate etched for 2 minutes with standard etch procedure using 1.5 vol % bromine in methanol.

bromine-methanol concentrations studied (0.3 to 10 vol %). The sizes of the defects ranged from 8 to 70 µm. These defects were present after 80 µm of the substrates were etched and probably exist throughout the wafers. A study showed that the same defects persisted for at least 30 µm into the wafer. Figure 5 depicts a typical defect after 50 µm of the substrate has been removed and the same defect with the removal of an additional 30 µm. A study with



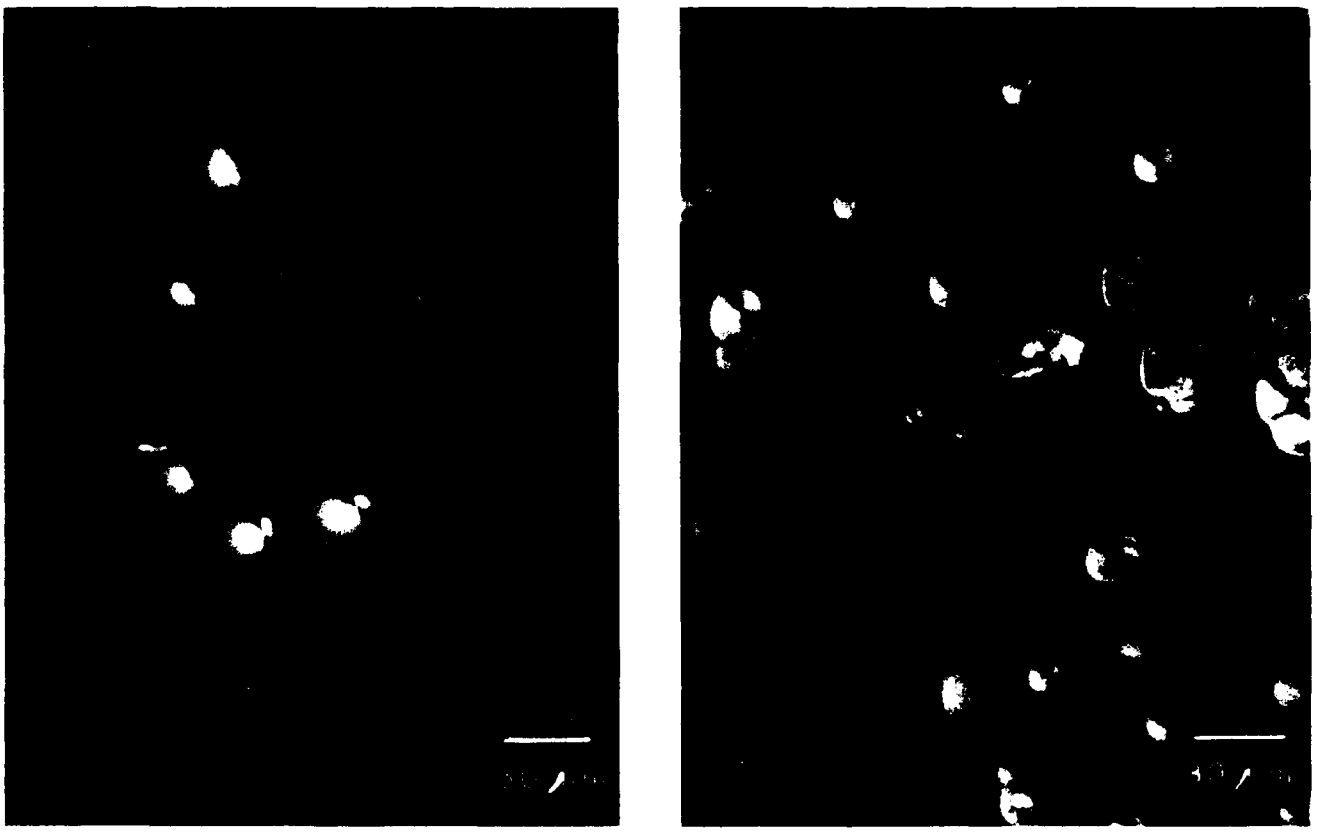
(a) (b)

Figure 5. Tenacity of Unspecified Defects in InP Substrates. a) Photomicrograph of CrystaComm InP substrate etched for 2 minutes with standard etch procedure using 10 vol % bromine in methanol; b) Photomicrograph of substrate in Figure 5a etched for an additional 2 minutes with standard etch procedure using 10 vol % bromine in methanol.

Huber's etch indicated that these defects are not associated with dislocations. These results are shown in Figure 6 where the defects are shown before and after treatment with Huber's etch. The origin of these defects may be a precipitate, inclusion, or areas with non-stoichiometric composition. Other Sumitomo substrates with an orientation of (100) $\pm$ 0.5° exhibited the same defects.

The number of these unspecified defects on the different substrates wafers were determined and are reported in Table 2. Defect values are reported after one and two 3 vol % bromine-methanol etches. The defect densities are observed to be of the same magnitude after the first etch. After the second etch with the 3 vol % bromine-methanol, CrystaComm and ICI Americas substrates show an increase in defect density with ICI Americas exhibiting a greater increase. The number of unspecified defects on the Sumitomo substrate remained relatively constant with the two etches. A second sample of the CrystaComm substrates showed a decrease in unspecified defects from 350 defects/cm^2 after a 1 vol % bromine-methanol etch to 130 for a second etch with 3 vol % bromine-methanol. These results indicate that these defect

densities vary as a function of depth but not in any one direction. Since the substrates displayed such variations in defect densities with the same relative magnitude, little or no significance can be attributed to the numerical difference.



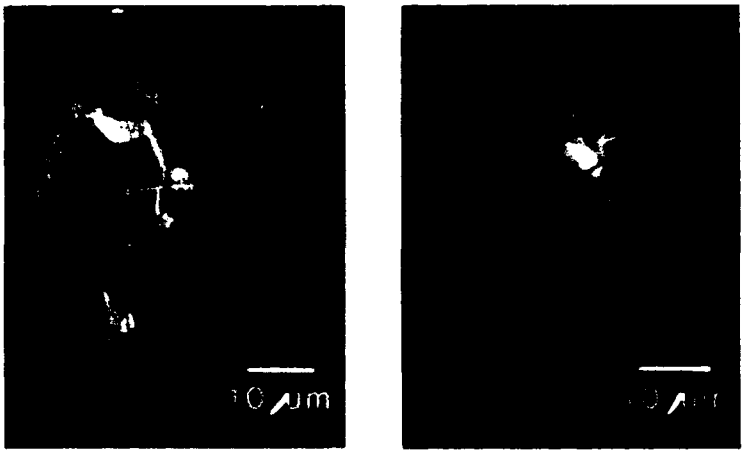
(a) (b)

Figure 6. Effect of Huber's Etch on Unspecified Defects. a) Photomicrograph of CrystaComm InP substrate etched for 2 minutes with standard etch procedure using 3 vol % bromine in methanol; b) Photomicrograph of substrate in 6a after etching with Huber's etch (2 volumes H_3PO_4 / 1 volume HBr) for 2 minutes.

Table 2. Number of Defects/cm^2 Observed after Bromine Etches for Different Substrates.

	Substrates		
	CrystaComm	ICI	Sumitomo
Defects/cm^2 after 3 percent bromine etch	210	260	190
Defects/cm^2 after 2nd 3 percent bromine etch	260	770	200

Small numbers of other defects were randomly observed on all the substrates after the standard etch procedure with the Br_2-methanol solutions. These defects displayed various features, for example, ridges, swirls, defects looking like broken blisters, and furrows. These broken-blister type defects are shown in Figure 7. No one substrate exhibited any more or less of these imperfections.



(a) (b)

Figure 7. Examples of Broken Blister-Type Defects on InP Substrates. a) Photomicrograph of CrystaComm InP substrate etched for 2 minutes with standard etch procedure using 3 vol % bromine in methanol; b) Photomicrograph of Sumitomo InP substrate etched for 2 minutes with standard etch procedure using 3 vol % bromine in methanol.

The subsurface damage on the indium phosphide substrates was investigated with Chu's etchant (3 volumes HBr: 1 volume HNO_3). The damage consisted primarily of scratches, swirls, and unspecified structures. The unspecified structure type of damage is depicted in the microphotograph in Figure 8. Scratches occurred more frequently than either swirls or unspecified structures. The amount of the subsurface damage on all the substrates was relatively small and typical values are presented in Table 3. CrystaComm exhibits a slightly greater number of scratches, swirls and defects than either ICI Americas or Sumitomo. ICI Americas and Sumitomo have approximately the same magnitude of damage. The results in Table 3 represent only the damage observed in the present study on the center rectangular samples of three different wafers from each of the commercial sources. Different values may be observed for other wafers from the same or different boules. Since Chin and Barlow[3] processed wafers with no subsurface damage with their polishing technique, one concludes that manufacturers should be able to produce substrates free of subsurface damage.

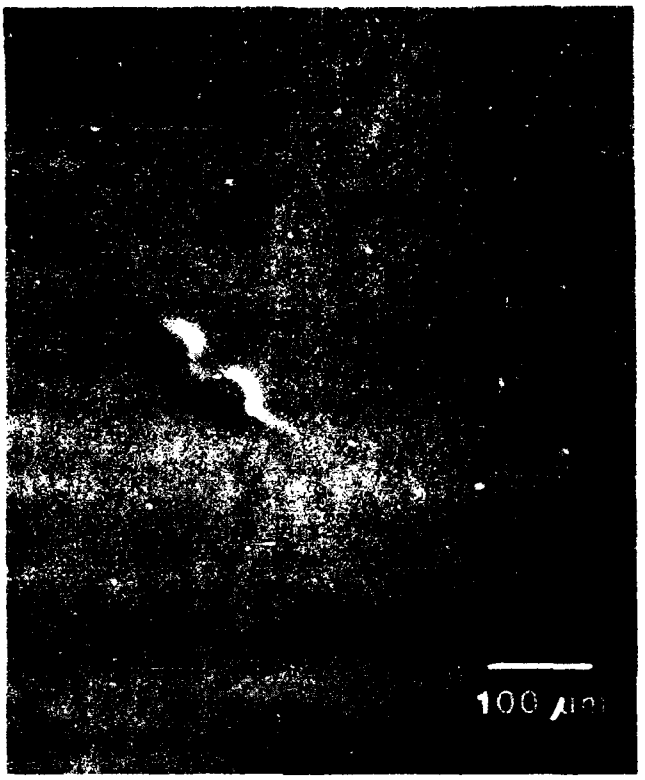


Figure 8. Example of Unspecified Subsurface Structure on Indium Phosphide Substrate Surface. Surface etched for 2 seconds with Chu's etch. Substrate source: ICI Americas.

Table 3. Subsurface Damage on Different Substrate Wafers.

Substrate Wafer	Number of Scratches, Swirls and Defects/cm^2
ICI Americas	~70
CrystaComm	~160
Sumitomo	~60

The small amount of subsurface damage on the wafers was verified from the results of the study of etch rates as a function of wafer depth. Tuck et al.[8,9] have shown that the depth of subsurface damage can be determined from plots of etch rates vs wafer depth. These investigators demonstrated that the etch rates of InP wafers containing damage was lower with bromine-methanol etching than the steady-state etch rate. Figure 9 depicts the etch rates determined for the three commercial substrates with 0.1 vol % bromine in methanol at various wafer depths. The plot shows that the etch rates determined at the different wafer depths were relatively constant (0.76 μm/min.) indicating that there was insufficient damage on the wafers to affect the etch rate. Tuck et al.[8] reported the depth of subsurface damage on a (100) surface of a InP wafer as 8 μm.

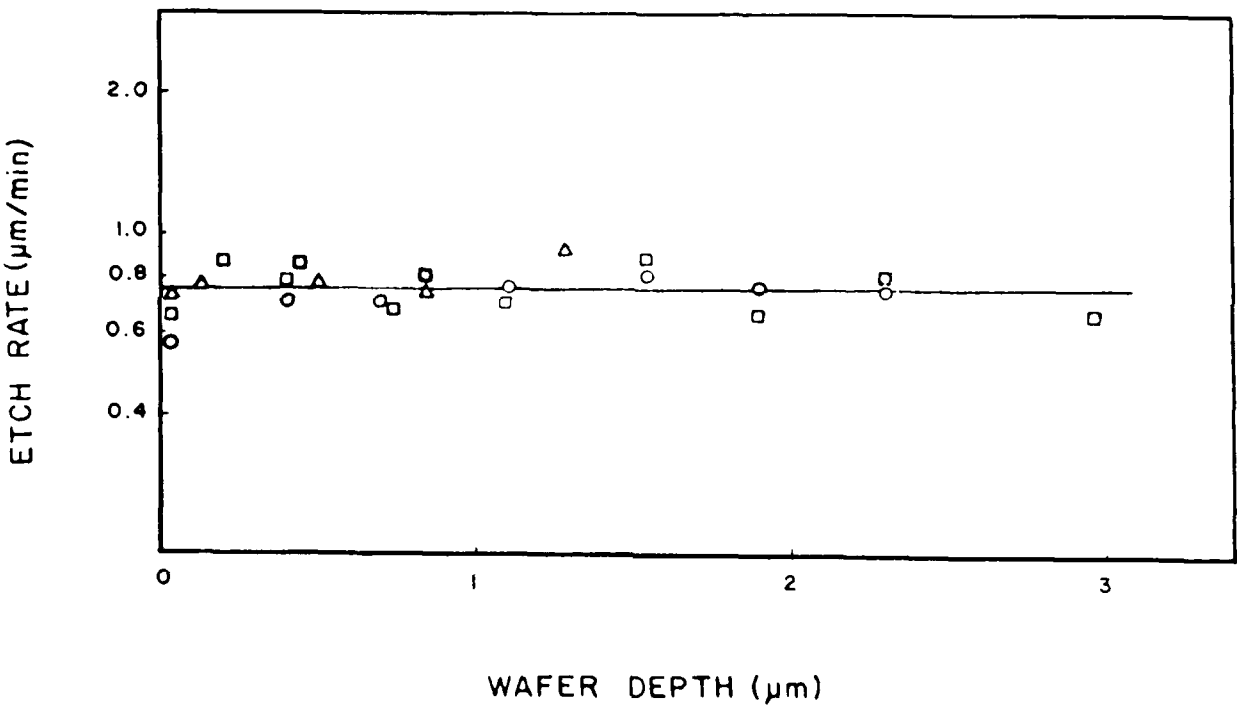


Figure 9. Etch Rates of Three Commercial Indium Phosphide Substrate Wafers as a Function of Wafer Depth. Etchant: 0.1 vol % bromine in methanol. Temperature: 25.0 ± 0.1°C. 0-0, ICI Americas; □-□, CrystaComm; Δ-Δ, Sumitomo.

4. SUMMARY

A comparison study of substrates from the three commercial sources, CrystaComm, ICI Americas and Sumitomo, is reported. The following defects and subsurface damage, revealed with the specified etchants, were studied: (i) Dislocations, 1 vol HBr with 2 vol H_3PO_4 (2 min); (ii) Speckles, < 1.5 vol % Br_2 in methanol (2 min); (iii) Unspecified Defects, ≥ 0.3 vol % Br_2 in methanol (2 min); and (iv) Subsurface Damage, 3 vol HBr with 1 vol HNO_3 (2 sec). The results showed that the substrates from the three commercial sources were of similar quality. Further InP technology research is needed in order to attain high quality InP substrates.

References

1. Olsen, G.H., and Zamerowski, T.J. (1980) *Progress in Crystal Growth and Characterization*, B.R. Pamplin, Editor, p. 309, Pergamon Press Ltd., London.

2. Caldwell, P.J., Laidig, W.D., Lin, Y.F., Peng, C.K., Magee, T.J. and Leung, C. (1985) *J. Appl. Phys.*, **57**:984.

3. Huber, A., and Linh, N.T. (1975) *J. Crystal Growth*, **29**:80.

4. Olsen, G.H., and Zamerowski, T.J. (1981) *IEEE J. Quantum Electron.*, **QE-17**, pp. 128-138.

5. Erstfeld, T.E., and Quinlan, K.P. (1982) *J. Electron. Mater.*, **11**:647.

6. Chu, S.N.G., Jodlauk, C.M., and Ballman, A.A. (1982) *J. Electrochem. Soc.*, **129**:352.

7. Chin, B.H., and Barlow, K.L. (1988) *J. Electrochem. Soc.*, **135**:3120.

8. Tuck, B., and Baker, A.J. (1973) *J. Mater. Sci.*, **8**:1559.

9. Tuck, B. (1975) *J. Mater. Sci.*, **10**:321.

10. Brown, G.T., Cockayne, B., and MacEwan, W.R. (1980) *J. Mater. Sci.*, **15**:2539.

11. Brown, G.T., Cockayne, B., and MacEwan, W.R. (6-10 April 1981) Microsc. Semicond. Mater. Conf., Inst. Phys. Conf., Ser. No. 60, Section 7, Oxford, pp. 351-356.

12. Jordan, A.S., Caruso, R., and Von Neida, A.R. (1980) *Bell. System Tech. J.*, **59**:593.

13. Chen, R.T., and Holmes, D.E. (1983) *J. Crystal Growth*, **61**:111.

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15. Tuppen, C.G., and Conen, B.H. (1987) *J. Crystal Growth*, **80**:459.

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